PB83-171843

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Illinois Univ. at Urbana-Champaign

Prepared for

Municipal Environmental Research Lab.
Cincinnati, OH

Dec 82

U.S. Department of Commerce
National Technical Information Service
NTIS

United States
Environmental Protection
Agency

Municipal Environmental Research
Laboratory
Cincinnati OH 45268

PB83-171843

Research and Development EPA-600/D-82-256 Dec. 1982

EPA ENVIRONMENTAL RESEARCH BRIEF

Reaction of Activated Carbon with Aqueous Chlorine and Chlorine Dioxide

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Abstract

The objective of this research was to determine whether aqueous chlorine and chlorine dioxide react with activated carbon, or with compounds absorbed on activated carbon, to produce compounds that would not form in the absence of activated carbon. The experimental conditions were either typical of those found in drinking water treatment plants, or they permitted conclusions to be made about the nature of the reaction under water treatment plant conditions.

Free chlorine is rapidly reduced to chloride by activated carbon. Extraction of carbon after reaction showed that compounds such as toluene, benzaldehyde, and benzoic acid were formed, but they were not found in the column effluent under water treatment plant conditions. Reaction with an amount of chlorine far exceeding that experienced in drinking water treatment leads to the formation of chloroform and other compounds, as well as a high molecular weight, chlorinated, dark colored product — all of which are eluted from the column.

Hypochlorous acid (HOCl) reacted with adsorbed humic substances to produce chloroform and other compounds, but the amount of chloroform formed per unit mass of HOCl reacted was less than that found when the reaction took place in the absence of carbon. Apparently the carbon destroys much of the HOCl that otherwise would have reacted with the humic substances. HOCl also reacted with adsorbed phenolic acids — including vanillic acid, syringic acid, and *p*-hydroxybenzoic acid that are structural breakdown products of humic substances — to produce a variety of polyphenols and quinones that were not formed in the absence of carbon.

Chlorine dioxide (ClO_2) also rapidly reacts with virgin carbon. When small amounts react such as would be expected in drinking water treatment plants, it appeared that all of the ClO_2 was converted to Cl^-. Some evidence was found that chlorate (ClO_3^-) was also formed when greater amounts reacted. No extractable oxidation products were, however, identified on the carbon surface.

The ClO_2 reaction with hydrocarbons such as ethylbenzene, indan, tetralin, diphenylmethane, and fluorene at pH 3.5 gave oxidized derivatives such as ketones and (sometimes) alcohols. In the presence of activated carbon, monochloro and/or dichloro derivatives were produced under some conditions in addition to the oxygenated compounds observed in the absence of carbon.

Byproducts of ClO_2 reactions in water by chlorite (ClO_2^-) and ClO_3^-. Virgin carbon readily reacts with ClO_2^-, although its capacity for reaction was sharply reduced after 80 to 90 mg ClO_2^-/g carbon had reacted. The reaction between ClO_2^- and adsorbed vanillic acid produced many unique organic products, whereas no reaction took place in the absence of carbon. ClO_3^- is inert on the carbon surface, however, and does not react except for a small amount of uptake by ion exchange.

This Research Brief was developed by the principal investigators and EPA's Municipal Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in the reports and publications listed on the end.

Introduction

Activated carbon, both powdered and granular, is frequently contacted by both organic compounds and

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SPRINGFIELD, VA. 22161

residual chlorine when it is used in water treatment. Carbon is an effective adsorbent of trace organic substances and is also a very effective reductant of free and combined chlorine. Although much work has been devoted to these separate roles of carbon, little attention has been given to studying the combined effects of chlorination and adsorption. For example, chlorine may react with activated carbon or with organic compounds adsorbed on carbon to produce compounds not normally found in aqueous chlorination reactions. It has been shown by others that activated carbon can promote many kinds of reactions including redox processes, peroxide decomposition, substitution, racemization, and *cis-trans* isomerization. Carbon will also possibly participate in the reactions of organic compounds with chlorine.

Chlorination, as normally practiced in water and wastewater treatment, results in the formation of trihalomethanes and other chlorinated organic compounds that may be undesirable from the viewpoint of water pollution control and human health. Accordingly, alternatives to chlorine for the disinfection of water and wastewater are being sought; ClO_2 is one disinfectant that has received considerable attention as an alternative disinfectant to chlorine. It is currently used at many water treatment plants to oxidize taste- and odor-causing compounds, and if it were to be substituted for chlorine as a predisinfectant, the likelihood of it contacting activated carbon and compounds adsorbed on carbon will be much increased. Thus, it is important that the reactions that will take place when this contact occurs also be identified. Whenever ClO_2 is used, ClO_2^- and ClO_3^- are also formed. Thus, the reactions of these species were also examined.

The experiments used in this research were designed so that the results could be used to show what products would likely form at drinking water treatment plants. Given that potentially harmful compounds formed on carbon can escape to the product water, it will be most important to prevent contact between these disinfectants and carbon during drinking water purification. It was not possible to study all aspects of the problem during this research project, but the results obtained do show that compounds formed when carbon is present do not form in aqueous solution when carbon is absent.

Free Chlorine-Activated Carbon Reaction

Free chlorine solutions prepared by bubbling chlorine gas into distilled, deionized, and purged water was reacted with activated carbon that had been baked at 175°C for 1 week to remove volatile compounds. Application of a 10 mg/L, pH 5.6 to 6, free chlorine solution to a column of granular activated carbon (GAC) until 0.1 g chlorine as Cl_2/g GAC had reacted showed no volatile compounds in the column effluent at concentrations greater than were in the influent. Extraction of the carbon showed that toluene, benzaldehyde, benzoic acid, 2-methoxyfluorene, and benzalacetophenone were formed, but they were not found in the column effluent. A greater extent of reaction at pH 7 to 8, 1.3 to 4.5 g as Cl_2/g GAC, led to the appearance of a dark-colored compound in the effluent and up to 50 μg/L chloroform in the column effluent.

A chlorine solution of approximately 500 mg/L as Cl_2 was reacted with carbon, and the colored product thus produced was concentrated and separated for analysis. The H, N, and S composition was similar to that of the virgin carbon, but the C content was much lower and the O and Cl contents much higher than virgin carbon. The molecular weight of the product was very great (100,000 to 300,000 MW as determined by ultrafiltration), and it was shown to be nonmutagenic to several *Salmonella* and *E. coli* test systems. This product is not expected to be formed under drinking water treatment conditions, and its presence in drinking water has never been reported (6).

Batch reactions at a very high dosage of free chlorine (2.5 g as Cl_2/g of carbon) produced several chlorinated organic compounds, including chloroform, trichloroethane, and several chlorinated aromatics. Nonchlorinated aromatic compounds, such as benzene and toluene, also were produced. The production of chlorinated organic compounds was mostly favored at high pH, and benzene and toluene were produced in neutral and basic solution that had black color. The increases in concentrations of various organic compounds were quite marked; for example, chloroform was present at 2.7 mg/L in a pH 11.5 batch reaction (6).

For all column runs at lower (50 mg HOCl as Cl_2 or less/L) chlorine dosage, no volatile organic compounds were observed in the effluent before 2 g as Cl_2/g of carbon had been achieved. After this ratio, chloroform levels in the effluent were as large as 50 μg/L. Soxhlet extraction of the carbon from a column receiving 10 mg chlorine/L until 0.11 g of Cl_2/g of carbon had reacted indicated several nonchlorinated aromatics that were not present in the influent. Halogenated compounds were not produced and desorbed since the total organic halogen (TOX) of the effluent remained below a measurable concentration throughout the column run (6).

Determination of TOX profiles in carbon columns receiving chlorine solutions initially were hampered by interference of the ClO_3^- ion in the TOX test (1). Subsequent experiments showed the ClO_3^- interference could be eliminated if the sample to be combusted was first nitrate washed (2,4,5). A review of the development of the TOX test is given in reference 5. The TOX profiles that resulted when 10 mg HOCl as Cl_2/L, at pH 4.8, were applied showed that the TOX buildup at the inlet was high but that the TOX did not penetrate deeply into the column. However, when hypochlorite ion (OCL^-) at pH 8.2 to 8.5 was applied, TOX on the carbon developed much further into the bed. It was also found that more TOX was produced from OCl^- than from HOCl (7.0 vs. 2.8 mg as Cl/g as Cl_2 reacted) (5).

HOCl-Adsorbed Compound Reactions

Adsorption of humic acid on GAC followed by application of free chlorine resulted in the formation of chloroform, which then appeared in the GAC column effluent. However, reaction of chlorine under the same conditions except that carbon was not present resulted in much more chloroform per unit weight chlorine reacted. The free chlorine reacts with GAC as well as adsorbed humic substances; thus, much more chlorine was required to form a given amount of chloroform (7).

The compounds formed on the carbon surface were extracted, identified, and compared with the compounds formed in aqueous solution in the absence of carbon. The compounds in the aqueous solution were adsorbed on XAD-2 and then eluted. Many compounds were found to be

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/D-82-256	2.	3. RECIPIENT'S ACCESSION NO. PB83 171843
4. TITLE AND SUBTITLE REACTION OF ACTIVATED CARBON WITH AQUEOUS CHLORINE AND CHLORINE DIOXIDE		5. REPORT DATE Dec. 1982 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) V. L. Snoeyink, R. A. Larson, A. S. C. Chen, L. M. J. Dielmann III, W. F. McHie, J. J. McCreary, J. E. Quinn, and E. A. Voudrias		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Illinois Urbana, IL 60801		10. PROGRAM ELEMENT NO. BNC1A 11. CONTRACT/GRANT NO. R-805293
12. SPONSORING AGENCY NAME AND ADDRESS Municipal Environmental Research Laboratory, Cin.,OH Office of Research and Development U.S. Environmental Protection Agency Cincinnati, OH 45268		13. TYPE OF REPORT AND PERIOD COVERED Res. Brief - 1979-81 14. SPONSORING AGENCY CODE EPA/600/14

15. SUPPLEMENTARY NOTES

Project Officer: Alan A. Stevens - (513)684-7342

16. ABSTRACT

The objective of this research was to determine whether aqueous chlorine and chlorine dioxide react with activated carbon, or with compounds adsorbed on activated carbon, to produce compounds that would not form in the absence of activated carbon. The experimental conditions were either typical of those found in drinking water treatment plants, or they permitted conclusions to be made about the nature of the reaction under water treatment plant conditions.

Free chlorine is rapidly reduced to chloride by activated carbon. Extraction of carbon after reaction showed that compounds such as toluene, benzaldehyde, and benzoic acid were formed, but they were not found in the column effluent under water treatment plant conditions.

Hypochlorous acid (HOCl) reacted with adsorbed humic substances to produce chloroform and other compounds but the amount of chloroform formed per unit mass of HOCl reacted was less than that found when the reaction took place in the absence of carbon.

Chlorine dioxide (ClO_2) also rapidly reacts with virgin carbon. When small amounts react such as would be expected in drinking water treatment plants, it appeared that all of the ClO_2 was coverted to Cl^-. The ClO_2 reaction with hydrocarbons adsorbed on activated carbon produces monochloro and/or dichloro derivatives under some conditions.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS *(This Report)* UNCLASSIFIED	21. NO. OF PAGES 6
	20. SECURITY CLASS *(This page)* UNCLASSIFIED	22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

formed both in aqueous solution and on the carbon. Some dihydroxybenzene molecules and chlorinated dihydroxybenzene molecules were found only on the carbon, indicating that the carbon surface was affecting the reaction (7).

The influence of the carbon surface on chlorine — organic compound reactions at pH 6 was further examined using three phenolic acids: *p*-hydroxybenzoic acid, vanillic acid, and syringic acid — compounds that are structural breakdown products of humic acid and constitutents of natural water. Results showed a variety of polyphenols and quinones that were produced only on the carbon surface by decarboxylation of the aromatic ring, hydroxylation of the aromatic ring, demethylation of methoxy substituents, oxidation to quinones, and chlorine substitution reactions. The aqueous solution was extracted with both XAD-2 and carbon to ensure that these compounds were not present. A generalized reaction scheme for the vanillic acid — HOCl reaction on the carbon surface was proposed (3,8).The dihydroxybenzenes and chlorinated dihydroxybenzenes recovered from the carbon on which HOCl had reacted with humic substances probably resulted from similar reactions. (3,8).

Adsorption of Chlorinated Organic Compounds

Humic and fulvic acid solutions were chlorinated to produce solutions with a wide variety of chlorinated organic compounds. The solutions were then applied to columns of GAC to determine the usefulness of adsorbed TOX as a measure of adsorption efficiency and remaining capacity and to determine the relative adsorbability of chloroform and the rest of the organohalogen compounds (2,4). The adsorbed TOX profiles, determined by removing carbon samples at different column depths and measuring the TOX of these samples, were very sharp and sensitive to the amount of TOX applied. The applied TOX was more efficiently adsorbed than total organic carbon (TOC), but TOX broke through faster than the chloroform. Comparison of the TOX profiles with those obtained at Jefferson Parish from full-scale GAC filters showed that the latter were not as sharp but that adsorbed TOX would still be a useful measurement to control GAC filters (4).

ClO_2-Activated Carbon Reactions

Chlorine-free ClO_2 was prepared by purging ClO_2 from a solution of $NaClO_2$ and potassium persulfate ($K_2S_2O_8$) and collecting it in chilled, deionized, distilled water. Batch experiments at pH 3.5 using ClO_2 concentrations up to 400 mg/L did not result in formation of volatile compounds (as shown by a purge-and-trap procedure). The TOX of the solution in contact with the carbon was also near the detection limit. At these high ClO_2 concentrations, much (22% to 37%) of the ClO_2 was converted to ClO_3^-, with the rest apparently being reduced to Cl^-. Column tests with more dilute solutions (3.8 mg/L) again showed no production of volatile compounds; further, the only inorganic product with Cl was Cl^-. There were low concentrations of TOX on the GAC after the reaction was stopped, but it was far less than that observed for free chlorine for an equivalent extent of reaction. Soxhlet extraction of the carbon indicated three organic compounds that were not present in the influent, but none of them were halogenated compounds (9).

ClO_2 — Adsorbed Compound Reactions

The hydrocarbons used for reaction studies were ethylbenzene, indan, tetralin, diphenylmethane, and fluorene. Chlorine dioxide was shown to react rapidly with these compounds in dilute (*ca.* 0.6 mg/L, 5 x 10^{-6} *M*) aqueous solution at pH 3.5. Hydrocarbons with benzylic hydrogen atoms reacted, probably by radical pathways, to give oxidized derivatives such as ketones and (sometimes) alcohols at the benzylic positions. In the presence of activated carbon, monochloro and/or dichloro derivatives were produced under some conditions in addition to the oxygenated compounds observed in the absence of the carbon. Tests using the appropriate blanks showed that these compounds were not produced from the ClO_2-activated carbon reaction. Typical results are shown in Table 1 for ethylbenzene and tetralin. Similar data are available for the other compounds, and the reaction with indan was also evaluated at pH 5.3 and 7.0.

ClO_2^- and ClO_3^- Reactions with Activated Carbon and ClO_2^- Reaction with Adsorbed Compounds

ClO_2^- was reduced to Cl^- by activated carbon. One virgin carbon was tested, and it had a capacity for reaction of about 80 to 90 mg ClO_2^-/g GAC before the reaction rate was sharply reduced. The effect of adsorbed organic compounds, and reactivation, on this reaction remains to be determined (5,10).

A small amount of ClO_3^- was taken up by carbon, probably by ion exchange, but no oxidation-reduction reaction took place.

The reaction between ClO_2^- and adsorbed vanillic acid yielded several reaction products identifiable by GC/MS, but no products were found in the absence of carbon. The carbon seemed to promote hydroxylation, decarboxylation, ring cleavage and CO_2 addition reactions. The products formed are listed in Table 2.

Conclusions

Several disinfectant and disinfectant byproducts were found to react readily with activated carbon. Hypochlorous acid, HOCl, and hypochlorite ion, OCl^-, reacted to produce some organic byproducts, but none of these byproducts were found in the column effluent when chlorine dose and times of reaction conditions were used that are typical of drinking water treatment plants. Chlorine dioxide, ClO_2, and chlorite, ClO_2^-, also readily reacted with one virgin carbon, but few organic byproducts were formed from these reactions. Chlorate, ClO_3^-, did not react.

The reaction of HOCl, ClO_2, and ClO_2^- with adsorbed organic compounds resulted in the formation of organic products that were not found in the absence of activated carbon. Most of the concentration of these species appears to react with the activated carbon itself, but sufficient amounts react with adsorbed compounds to form organic products that can be measured. HOCl reacted with adsorbed humic substances and a variety of adsorbed phenolic compounds to produce several polyphenols and quinones that were not formed in the absence of carbon. Adsorbed hydrocarbons reacted with ClO_2 to form halogenated compounds and ClO_2^- reacted with adsorbed vanillic acid to produce more

Table 1. Chlorine Dioxide-Hydrocarbon Reactions at pH 3.5

Compound	Mol. Wt.	Aqueous Soln[a]	Carbon Extract[b]
ETHYLBENZENE			
1. ethylbenzene[c]	106	+	+
2. acetophenone	120	+[f]	+[f]
3. α-methylbenzyl alcohol	122		+
4. methyl-2-(or 3-) chlorobenzoate	170		+
5. α-phenylethylether[d]	226		+
TETRALIN			
1. *cis*-decalin[e]	138	+	+
2. *trans*-decalin[e]	138	+	+
3. tetralin[c]	132	+	+
4. naphthalene[e]	128	+	+
5. 1,2-dihydronaphthalene	130		trace
6. β-o-hydroxyphenylpropionic acid	166	?	
7. α-tetralone	146	+[f]	+[f]
8. α-tetralol	148	+	+
9. α-naphthoquinone	158	+[f]	
10. hydroxy-1-tetralone or hydroxycoumarin	162	+	
11. α-tetralone monochloro derivative	180		+
12. α-tetralol monochloro derivative	182	+	
13. tetralin dichloro derivative			trace
14. β-o-carboxyphenylpropionic acid methyl ester	222		+

[a] XAD-2 extracts of aqueous solutions reacted for 2.9 min, 1 hr, and 2 days.
[b] Soxhlet extraction of 2 g of carbon receiving a reaction mixture of chlorine dioxide and hydrocarbon reacted for 2.9 min.
[c] Starting material.
[d] From ClO_2-GAC reaction.
[e] Impurity
[f] Major product.
[g] Reaction product of impurity.

oxygenated compounds that were not formed in the absence of carbon.

Additional studies are needed to characterize the types of reactions that occur between disinfectants and compounds adsorbed on activated carbon, and to determine whether those products that are formed can be displaced into the product water in significant concentration. When such data are available, it will be possible to make an informed decision about whether selected disinfectants should be permitted to contact activated carbon when certain species of adsorbed compounds are likely to be present.

References

The following papers and reports contain the findings of this research project in their entirety. The Ph.D. thesis (#3) is available from University Microfilms, P.O. Box 1346, Ann Arbor, MI 48106. The M.S. theses (#1,2,5) are available from the University of Illinois Library or Vernon L. Snoeyink, Department of Civil Engineering, University of Illinois, 208 North Romine, Urbana, IL 61801. The articles that are in press or preparation (#8,9,10) are also available from Vernon L. Snoeyink until they appear in the journals.

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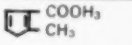
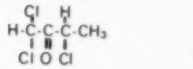
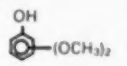
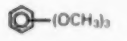
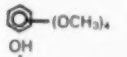
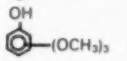
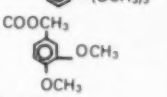
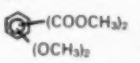
Table 2. Compounds Identified for the Reaction between Vanillic Acid and Chlorite in the Presence of Carbon

Peak #	Structure	Name	Mol. Wt.
1.		2-Methyl-3-Furancarboxylic acid methylester	140
2.		1,1,3(or 1,1,4)-trichloro 2-butanone	174
3.		Dimethoxyhydroxybenzene	154
*4.		Trimethoxybenzene	168
*5.		Tetramethoxybenzene	198
*6.		Trimethoxyhydroxybenzene	184
7.		Methylated vanillic acid	196
8.	Unknown		222
9.	Unknown		220
10.	Unknown		206
11.	Unknown		220
12.	Unknown		234
13.	Unknown		222
14.		Dimethoxybenzene dicarboxylic acid dimethylester	254
15.	Unknown		235
16.	Unknown		208

*Indicates that the compound has been found in the vanillic acid-free chlorine-carbon reaction (McCreary, 1980).

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☆U. S. GOVERNMENT PRINTING OFFICE: 1983/659-095/0563